Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Color tuning of di-boron derived TADF emitters: molecular design and property prediction

Jiaqi Li, Fei Zhao, Yanan Chen, Mingfan Zhang, Tingyu Li, and Houyu Zhang*

State key laboratory of supramolecular structure and materials,

Institute of theoretical chemistry, College of Chemistry, Jilin university,

Changchun 130012, P.R. China

*Email: houyuzhang@jlu.edu.cn

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Table S1 Calculated HOMO energies (eV) of molecule **1a** in dichloromethane solution and in gas phase (in parentheses) with different DFT functionals with a fixed percentage of nonlocal Hartree-Fock exchange (**HF_{exc}**).

	B3LYP	PBE0	BMK	CAM-B3LYP	Exptl.[a]
HF_{exc}	**20%**	**25%**	**42%**	**19% at SR and 65% at LR**	
HOMO	-5.41 (-5.25)	-5.69 (-5.51)	-6.14 (-5.97)	-6.55 (-6.55)	-5.57

[a]From ref 25.

Table S2 Calculated absorption wavelength (λ_{abs}) of molecule **1a** in toluene solution and the emission wavelength (λ_{em}) in gas environment with different DFT functionals with a fixed percentage of nonlocal Hartree-Fock exchange (**HF_{exc}**).

	B3LYP	PBE0	BMK	CAM-B3LYP	Exptl.[a]
HF_{exc}	**20%**	**25%**	**42%**	**19% at SR and 65% at LR**	
λ_{abs} (nm)	379	359	332	300	342
	564	517	421	362	425
λ_{em} (nm)	711	638	531	437	524

[a]From ref 25.

Table S3 Calculated AIP and VIP (in parentheses) values (eV) with PBE0 functional and calculated λ_{abs} and λ_{em} with BMK functional for molecule **1b** in gas phase.

1b	Calculated values	Exptl.[b]
AIP (VIP)	5.33 (5.36)	5.56
λ_{abs} (nm)	485	480
λ_{em} (nm)	584	587

[b]From ref 26.

Table S4 Calculated HOMO and LUMO of the electron-donating fragments CZ and DMAC by DFT at the PBE0/6-31G(d, p) level.

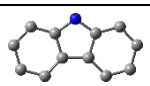
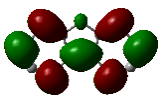
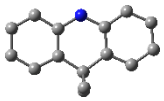
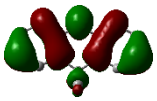
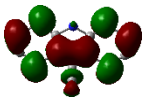
Donor	Structure	HOMO		LUMO	
CZ			-5.73 eV		-0.56 eV
DMAC			-5.13 eV		-0.05 eV

Table S5 Calculated HOMO and LUMO of the different electron-withdrawing units by DFT at the PBE0/6-31G(d, p) level.

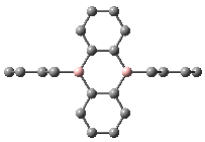
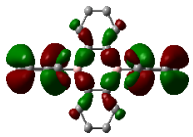
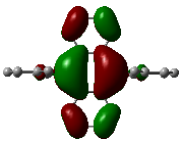
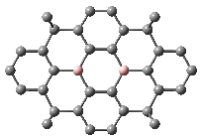
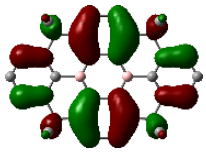
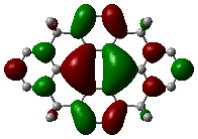
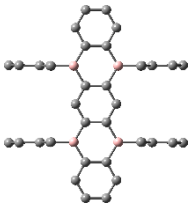
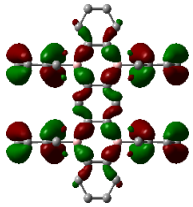
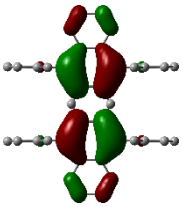
Acceptor	Structure	HOMO		LUMO	
1			-6.39 eV		-2.46 eV
2			-6.34 eV		-2.07 eV
3			-6.32 eV		-2.96 eV

Table S6 Calculated absorption excited energies, dominant orbital excitations, oscillator strengths and absorption wavelengths from TD-DFT calculations for the molecules in toluene solvent.

Molecule	State	Δ*E* (eV)	Excitation	λ_{abs} (nm)	*f*
1a	S_1	2.9445	H → L (83%)	421.1	0.0008
	S_{10}	4.0313	H-11 → L (82%)	307.6	0.1764
	S_{12}	4.3214	H → L +3 (45%)	286.9	0.1936
			H-1 → L +2 (44%)		
	S_{18}	4.7402	H → L +4 (42%)	261.6	1.1354
			H-1 → L +5 (40%)		
	S_{36}	5.6175	H-2 → L +4 (29%)	220.7	0.7955
			H-3 → L +5 (28%)		
1b	S_1	2.7057	H → L (100%)	458.2	0
	S_8	2.5541	H-1→ L (100%)	485.4	0.0001
	S_{15}	4.4608	H-1 → L +5 (40%)	277.9	0.2062
			H-1 → L +6 (26%)		
	S_{28}	4.9302	H-15 → L (95%)	251.5	0.6599
	S_{33}	5.3174	H-10 → L +1 (82%)	233.2	0.9681
2a	S_1	3.2917	H → L (90%)	376.7	0.8692
	S_4	3.7653	H-4 → L (93%)	329.3	0.2739
	S_{11}	4.3349	H-8 → L (38%)	286.0	0.6258
			H → L +3 (26%)		
	S_{24}	5.1565	H-5 → L+1 (80%)	240.4	0.5135
	S_{30}	5.3398	H-1 → L +5 (41%)	232.2	0.2641
			H-6 → L +1 (28%)		
	S_{34}	5.4718	H → L +9 (34%)	226.6	0.8163
			H-1 → L +8 (32%)		

2b	S_1	2.8738	H → L (93%)	431.4	0.0038
	S_4	3.7360	H-2 → L (91%)	331.9	0.2924
	S_6	4.0706	H-8 → L (94%)	304.6	1.2396
	S_{18}	4.6447	H → L+8 (46%)	266.9	0.6060
			H-1 → L+7 (38%)		
	S_{32}	5.1464	H-4 → L +1 (87%)	240.9	0.5229
	S_{50}	5.9466	H → L +11 (28%)	208.5	0.1280
			H-7 → L +1 (21%)		
3a	S_1	2.3545	H → L (93%)	526.6	0
	S_{15}	3.5286	H-13 → L (58%)	351.4	0.1923
			H-21 → L (28%)		
	S_{19}	3.5924	H-21 → L (54%)	345.1	0.2398
			H-13 → L +1 (31%)		
	S_{40}	4.3003	H-1 → L +4 (31%)	288.3	0.3162
			H → L +5 (29%)		
	S_{49}	4.6351	H → L +8 (21%)	267.5	2.2638
			H-3 → L +9 (19%)		
			H-2 → L +10 (19%)		
3b	S_1	2.1612	H → L (99%)	573.7	0.0004
	S_{14}	3.4806	H-12 → L (59%)	356.2	0.0671
	S_{18}	3.5883	H-25 → L +1 (69%)	345.5	0.3043
	S_{34}	4.1155	H-29 → L +1 (60%)	301.3	0.0748
	S_{50}	4.4546	H-2 → L +11 (22%)	278.3	0.2700
			H-3 → L +10 (21%)		
			H-1 → L +8 (20%)		

Table S7 Calculated emission energies, dominant orbital excitations, oscillator strengths and emission wavelengths from TD-DFT calculations for the molecules.

Molecule	**State**	**Δ*E* (eV)**	**Excitation**	**λ_{em} (nm)**	***f***
1a	S_1	2.3342	H → L (90%)	531.2	0.0013
1b	S_1	2.1238	H → L (100%)	583.8	0.0001
2a	S_1	3.0721	H → L (90%)	403.6	0.5888
2b	S_1	2.5410	H → L (95%)	487.9	0.0007
3a	S_1	1.8861	H → L (95%)	657.4	0.0075
3b	S_1	1.6978	H → L (96%)	730.3	0.0005

Fig. S1 Schematic diagram of the potential energy surfaces and computational details for ΔE_{ST} and reorganization energies.

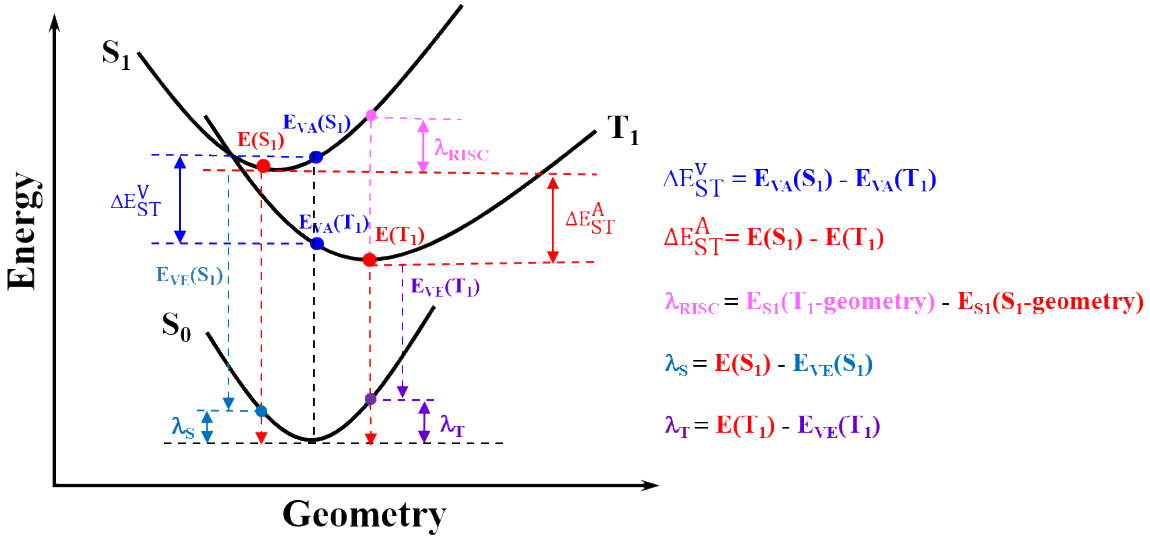


Fig. S2 H-H interatomic repulsion effect between donor unit and phenyl group.

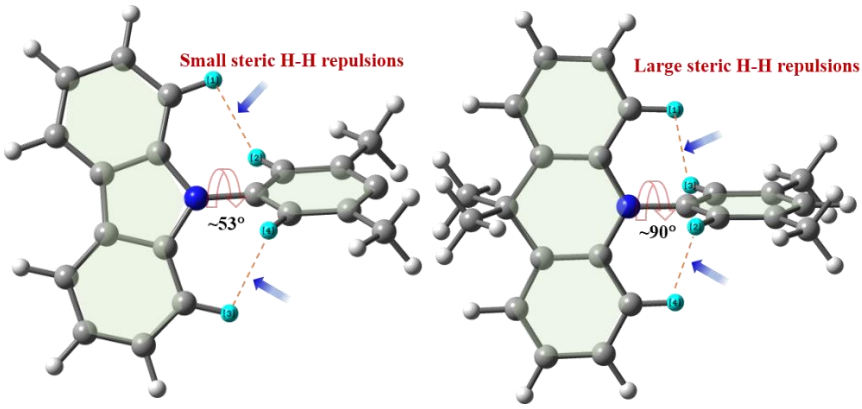


Fig. S3 Structural changes between the optimized structures of S_0 and S_1, S_0 and T_1, and S_1 and T_1 states (S_0, S_1, and T_1 structures are depicted in grey, red, and blue, respectively).

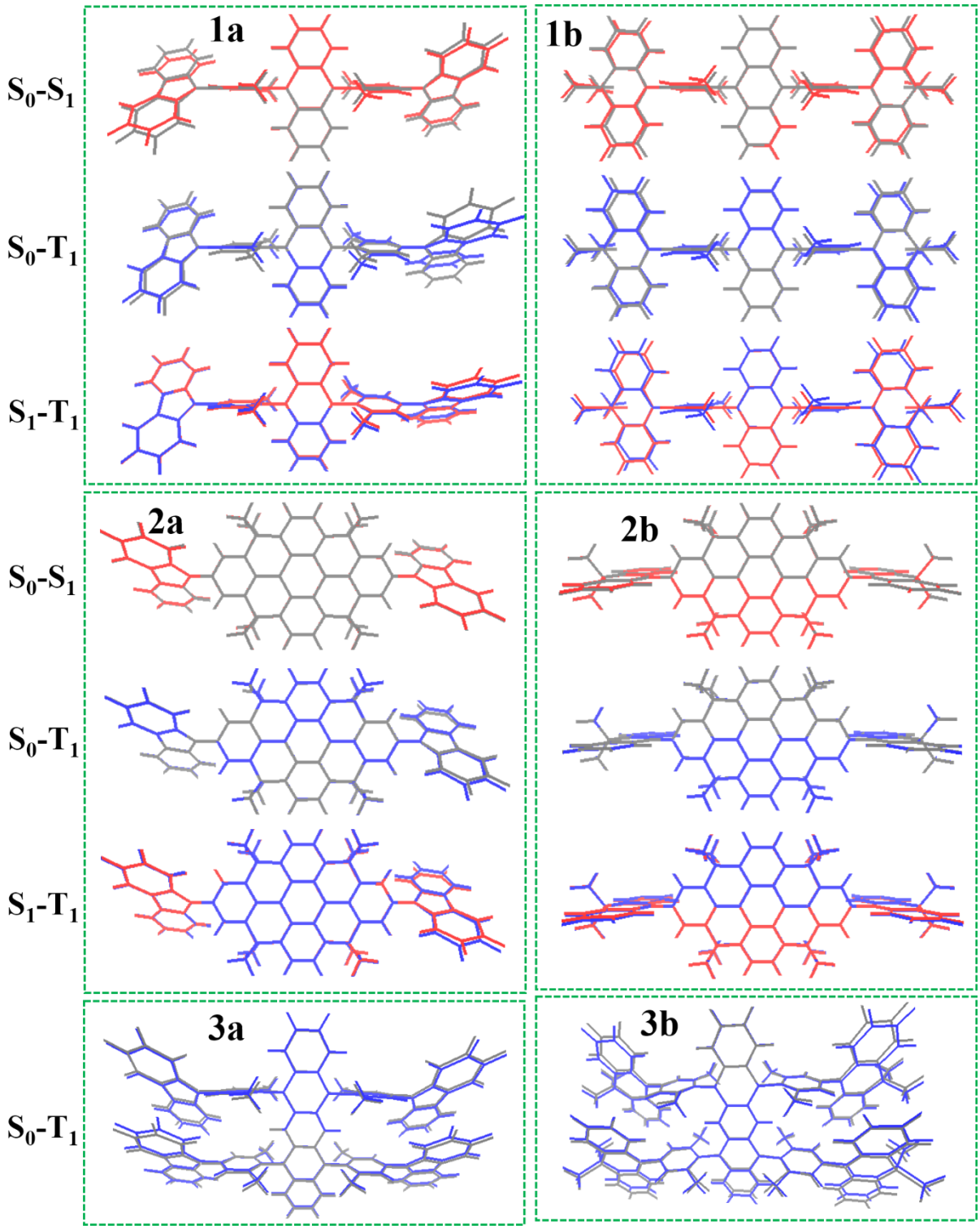


Fig. S4 Chemical structure (a) and optimized structure (b) of molecule **2a-Me**.

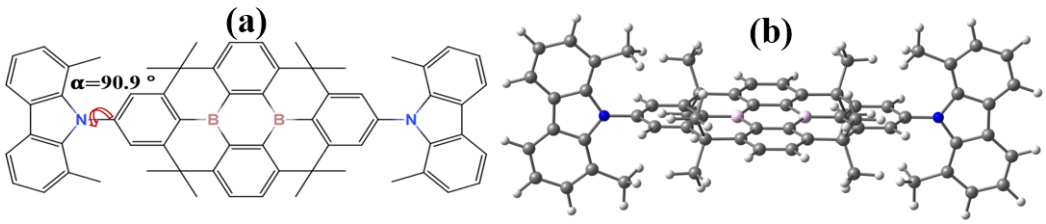


Fig. S5 Plots of the orbitals involved in the transitions for all molecules calculated at the BMK/6-31G(d, p) level (saturated H atoms are not shown).

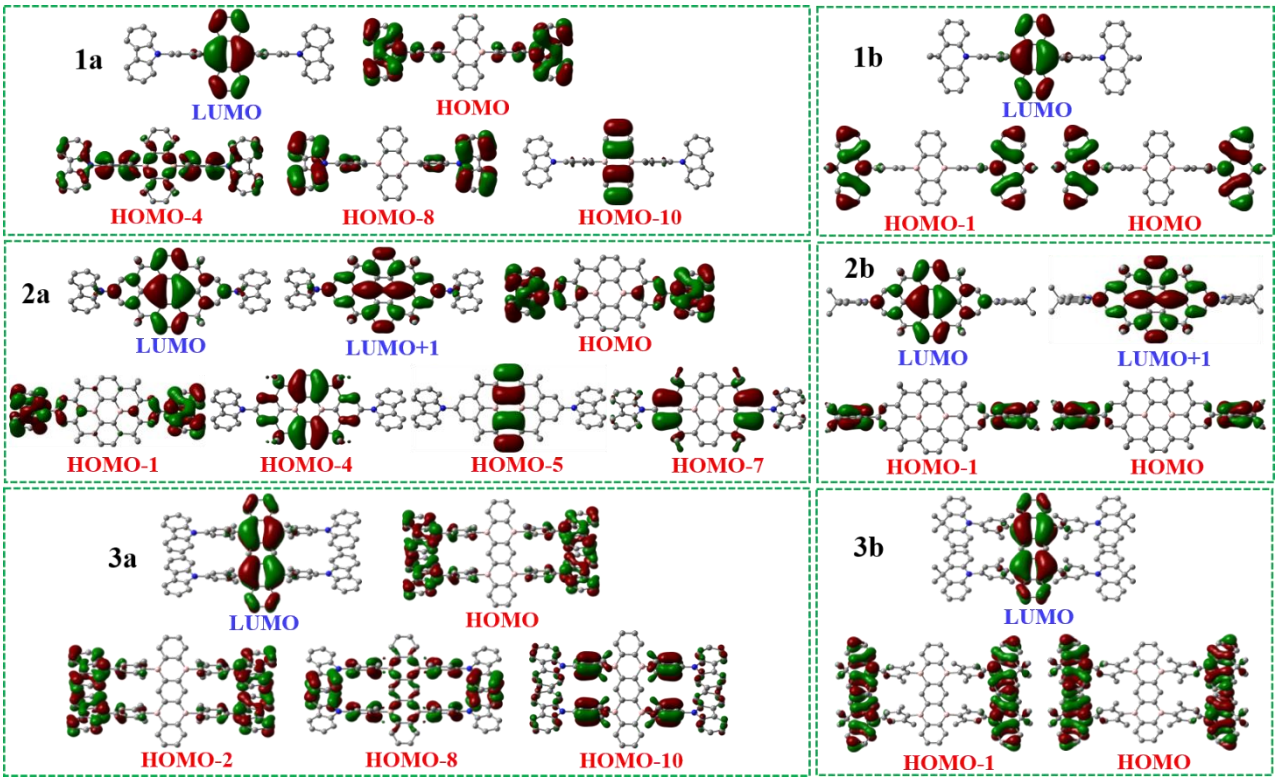


Fig. S6 NTO analysis for the S_1 and T_n excited states for molecules in series **2** and **3** (saturated H atoms are not shown).

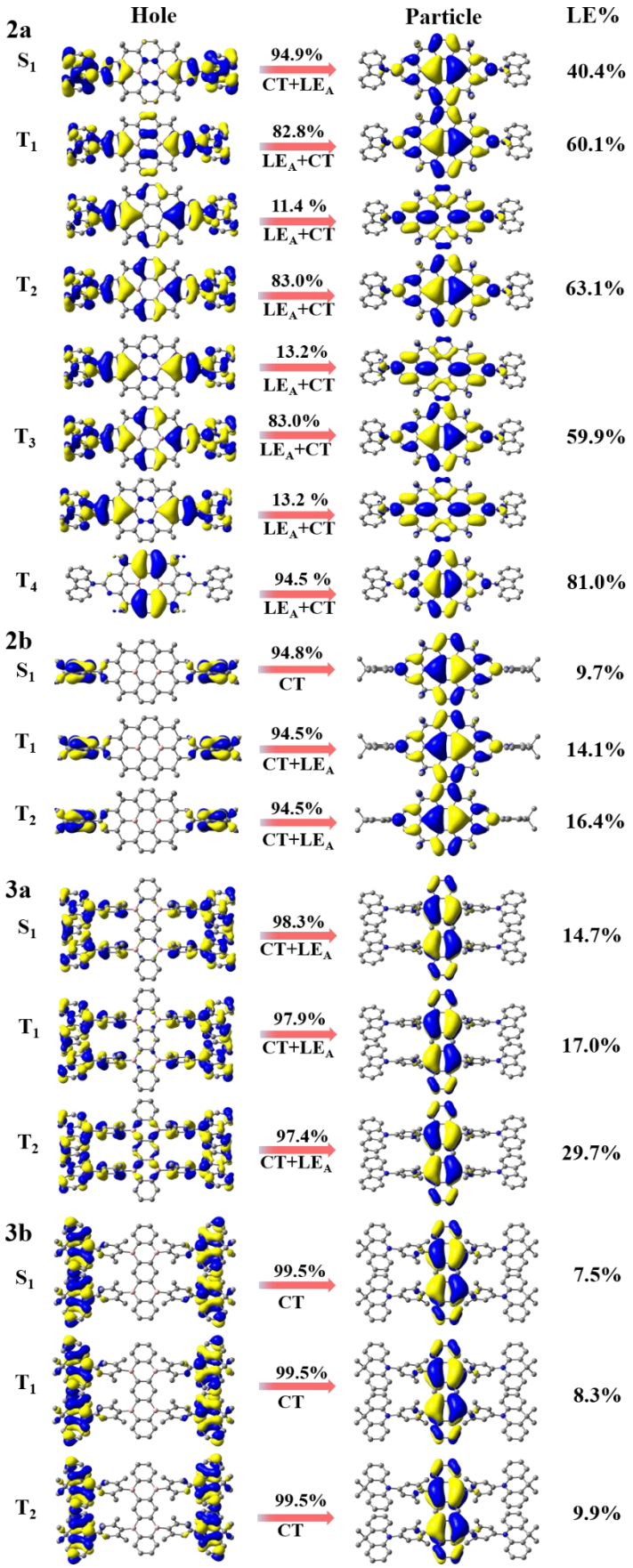


Fig. S7 NTO analysis for molecule **1b** at dihedral angle α = 60°.

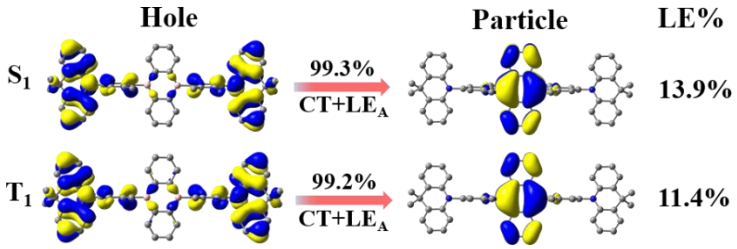


Fig. S8 Calculated TADF rate constants and NTO analysis for molecule **2a-Me**.

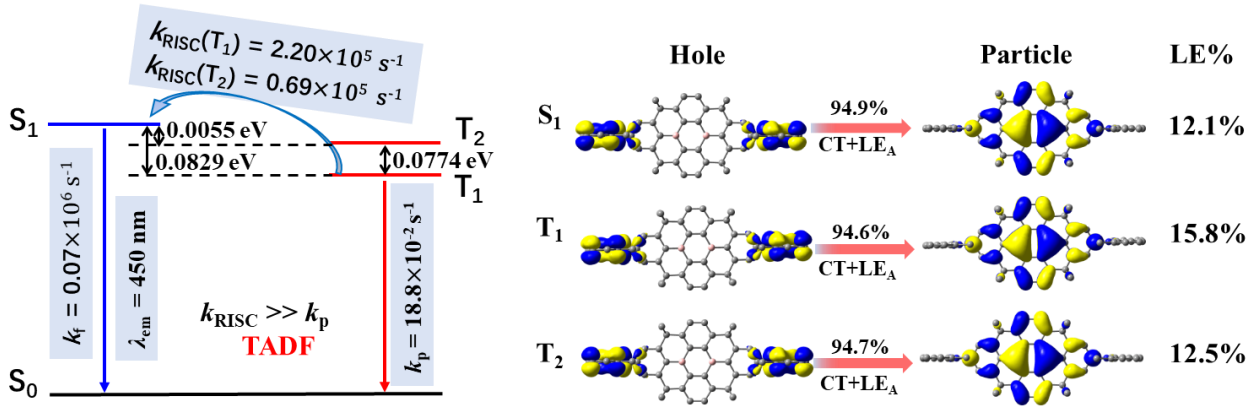


Fig. S9 Calculated relative energies and oscillator strengths in the S_1 state of molecule **1b** as function of the twisted angles. The blue dashed line labels the thermally activated energy (0.026 eV) at room temperature.